A Study of Catalytic Actions at Solid Surfaces.—IV. *The Interaction of Carbon Monoxide and Steam as Conditioned by Iron Oxide and by Copper.*

By E. F. Armstrong, D.Sc., F.I.C., and T. P. Hilditch, D.Sc., F.I.C.

(Communicated by Prof. H. E. Armstrong, F.R.S. Received March 18, 1920.)

The process summed up in the equation

$$CO + H_2O \rightleftarrows CO_2 + H_2 + 10{,}200 \text{ cal.}$$

is limited by the conditions which govern any homogeneous system in equilibrium: if the concentration of carbon monoxide, water, carbon dioxide, and hydrogen be denoted by a, b, c, d respectively, by the usual application of the law of mass action

$$k_1ab = k_2cd,$$

or

$$K = k_2/k_1 = ab/cd.$$

The value of K, the "equilibrium constant," depends on the temperature at which interaction takes place.

Haber* gives the following experimental values of K between 200° C. and 600° C.:—

Temperature.	227°.	327°.	400°.	500°.	600°.
K	0·006	0·03	0·05	0·16	0·32

These values, of course, define merely the extreme limits of composition of the gas-mixture, by whatever intermediate steps the transformation be effected. As a matter of fact, a mixture of carbon monoxide and steam at any of the temperatures mentioned, in the absence of a third agent, would attain equilibrium only after an exceedingly long time. It is well known, however, that many metallic oxides accelerate the attainment of equilibrium, specially prepared oxides of iron being very effective; the interaction has been utilised in the manufacture of hydrogen, the first attempt being that made by the Badische Anilin und Soda Fabrik in producing hydrogen for the Haber ammonia synthesis.

* 'Zeitschr. Physik. Chem.,' vol. 68, p. 731 (1909).

The action of the iron oxide may be represented as follows:—

$$(a)\ \begin{cases} CO + Fe_3O_4 \rightleftarrows CO_2 + 3FeO, \\ CO + FeO \rightleftarrows CO_2 + Fe, \end{cases}$$

$$(b)\ \begin{cases} H_2O + 3FeO \rightleftarrows Fe_3O_4 + H_2, \\ H_2O + Fe \rightleftarrows FeO + H_2, \end{cases}$$

or together

$$CO + H_2O + (Fe_3O_4 - FeO - Fe) \rightleftarrows (Fe_3O_4 - FeO - Fe) + CO_2 + H_2.$$

The action belongs to the same class as several others we have described in these papers, and may be regarded as proceeding by a series of chemical unions between the four agents and the iron oxide catalyst.

Our present object is to describe experiments which show that copper, specially prepared for use as a catalyst [the same material which served for our experiments (Part III of this series) upon the dehydrogenation of ethyl alcohol)], can also condition the transformation of carbon monoxide and steam into carbon dioxide and hydrogen. Whereas, however, iron oxide at a suitable temperature causes the action to proceed almost to the point of equilibrium, copper, even at its optimum temperature, does not effect more than 50–70 per cent. of the possible amount of chemical change; the exact proportion is to some extent a function of the composition of the mixture used.

These results are of considerable theoretical interest from the point of view of the general theory of catalysis which we have lately put forward, because they illustrate very beautifully the specific action of two different types of catalyst, effecting ultimately the same change ($CO + H_2O = CO_2 + H_2$), but, as we shall show, by an entirely different mechanism, involving the production of intermediate systems of quite distinct kinds.

At first sight, it might seem that the case was one in which no chemical change was involved, the process being in each instance merely due to physical adsorption or concentration of the acting gases at the active surface; but the evidence which we are about to quote on the relation of temperature to the amount of action produced is sufficient to negative this view.

It is obvious that copper cannot exercise the function we have elsewhere ascribed to iron oxide, as water has no detectable action on the copper catalyst, at all events up to 500° C.

Sabatier and Mailhe* have observed, on the other hand, that finely divided copper is capable of decomposing formic acid into carbon dioxide

* 'Compt. Rend.,' vol. 152, p. 1212 (1911).

and hydrogen from 190° C. upwards, and our experiments go to show that it is this specific property of copper which accounts for the results we have obtained. Apparently, there is a tendency to the equilibrium

$$CO + H_2O \rightleftharpoons H.COOH,$$

the balance being overwhelmingly in favour of the uncombined components, as indicated; in presence of copper the formic acid is partially or wholly removed in the sense

$$H.COOH \longrightarrow CO_2 + H_2,$$

so that ultimately a large proportion of the carbon monoxide is transformed into dioxide.

It is well known, of course, that under quite different conditions carbon monoxide will yield formates; for example, under high pressure and at a moderate temperature, this gas may be readily absorbed by caustic alkalies.

Again, K. A. Hofmann* has explained the oxidation, at the ordinary temperature, of carbon monoxide to dioxide at a copper surface moistened with alkali by assuming the formation of a labile isoformate, HO.C.OK; the production of this substance is only minimal under ordinary conditions but is stimulated in presence of copper.

We have succeeded in proving that a mixture of carbon monoxide and steam, under the conditions of our experiments (at about 350° C.) but in the absence of any catalyst, may give rise to the momentary formation of small but quite detectable quantities of formic acid. Thus, when ammonia was added to the gases before passing through the heated tube, in the expectation that some ammonium formate might remain undecomposed at the exit of the apparatus, this hope was realised, the aqueous condensate from the apparatus being found to blacken silver nitrate and to reduce neutral mercuric chloride solution to mercurous chloride. The amount of formic acid preserved was, of course, quite minute. A similar result was obtained when the carbon monoxide and steam were passed over lime at 350° C.; details of these experiments are given after the main series of experiments with copper and iron oxide catalysts have been described.

We have been chiefly concerned to examine the amount of the change

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

at temperatures from 200° C. to 500° C. with both copper and iron oxide catalysts. In order to standardise as far as possible the time-factor in the attainment of equilibrium, we have selected a rate of flow of gas such that the maximum change was effected over the most active range of temperature;

* 'Ber.,' vol. 51, p. 1526 (1918).

we then arranged for the same rate of flow at the other temperatures and noted the amount of carbon monoxide converted to dioxide.

Two samples of gas were used in the course of the work:

(a) "95 *per cent. CO-gas*" obtained from sodium formate and sulphuric acid; this gas was operated at a rate of 12 litres per hour.

(b) "40 *per cent. CO-gas*" ordinary water-gas, used at the rate of 25 litres per hour.

In all cases a mixture of one volume of the gas with approximately 2·5 volumes of steam was passed over the catalyst, the water vapour being picked up by the gas during its passage through a vessel containing agitated water maintained at a temperature adjusted to give the desired saturation of the gas with steam.

The limiting value of the amount of carbon monoxide which can be transformed is derived as follows:—

Let a, b, c, d, as before, be the original concentration (volumes) of carbon monoxide, water, carbon dioxide, and hydrogen. Then, if a volume-concentration s of carbon monoxide interact with steam

$$K = \frac{(a-s)(b-s)}{(c+s)(d+s)}.$$

Hence the theoretical values of s can be determined at each temperature for which K is given and also the corresponding ratio

$$s/a = \textit{amount of CO changed/original amount of CO.}$$

In the actual experiments, the change was followed by analyses of the entering and issuing gases other than water.

Let the concentrations of CO_2, CO and H_2 per unit volume in the original gas be respectively X, Y, and Z, and let y of the original CO be changed. After re-condensation of the steam, the volume of the gas is now $1+y$, and we have

$$\text{New concentration CO} = \frac{Y-y}{1+y}.$$

$$\text{New concentration } CO_2 = \frac{X+y}{1+y}.$$

$$\text{New concentration } H_2 = \frac{Z+y}{1+y}.$$

Gas-analysis furnished experimental values for the old and new percentages of CO, CO_2 and H_2, the CO estimation being considered to be the most accurate of the three.

Thus, from the measured new per cent. CO

$$y = \frac{\text{Y} - \text{new per cent. CO}/100}{1 + \text{new per cent. CO}/100}$$

and experimental values were deduced for

$$y/Y = \textit{amount of CO changed}/\textit{original amount of CO},$$

i.e., a figure comparable with the theoretical s/a above.

Further, an estimate of the accuracy of the analytical work was obtained by comparing the found and calculated new percentages of CO_2 and H_2 :—

$$\text{New per cent. } CO_2 \textit{ (calculated)} = 100 \cdot \frac{X+y}{1+y}.$$

$$\text{New per cent. } H_2 \textit{ (calculated)} = 100 \cdot \frac{Z+y}{1+y}.$$

I. 95 *per cent. CO—Gas.*

Composition of gas : 0·35 per cent. CO_2, 95·3 per cent. CO, 2·3 per cent. H_2. The theoretical data for this gas are as follows :—

1 vol. gas + 2·5 vols. H_2O,

$$a = 0{\cdot}272, \quad b = 0{\cdot}714, \quad c = 0{\cdot}001, \quad d = 0{\cdot}007.$$

Temperature.	227°.	327°.	400°.	500°.	600°.
K	0·006	0·03	0·05	0·16	0·32
s	0·271	0·268	0·263	0·250	0·234
s/a	0·997	0·983	0·966	0·919	0·860

Experimental data :—

Temperature.	Composition of issuing gas.			y.	y/Y.	Per cent. CO_2.	Per cent. H_2.
	Per cent. CO_2.	Per cent. CO.	Per cent. H_2.			Calculated from y.	
			(*a*) Reduced copper catalyst.				
200°	3·1	87·0	5·3	0·044	0·046	4·6	6·4
250	23·9	48·3	23·5	0·317	0·333	24·3	25·8
300	41·4	14·0	41·5	0·713	0·748	41·8	42·9
350	43·4	14·0	39·5	0·713	0·748	41·8	42·9
400	40·5	15·5	41·2	0·691	0·725	41·0	42·2
500	35·2	24·2	37·0	0·572	0·600	36·6	37·9
			(*b*) Iron oxide catalyst.				
250	9·6	70·4	14·0	0·146	0·153	12·2	14·8
300	27·9	35·1	26·2	0·446	0·468	31·9	32·4
350	45·6	4·2	45·8	0·874	0·917	46·8	47·9
400	47·0	2·4	47·0	0·907	0·952	47·7	48·8

The relations of y/Y to temperature, together with the corresponding values for s/a, are shown graphically in fig. 1.

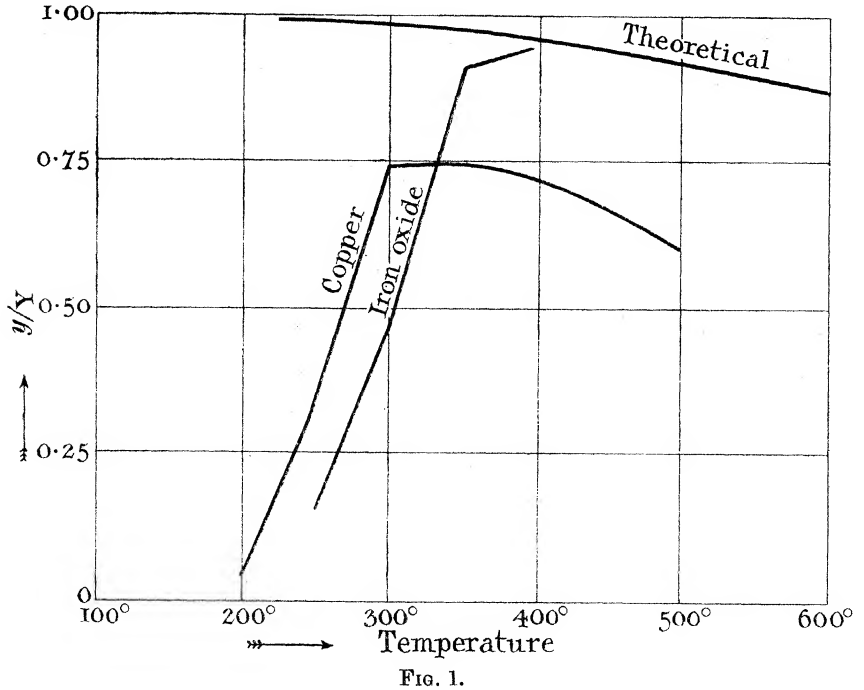

Fig. 1.

II. 40 *per cent. CO—Gas (Water-Gas).*

Average composition of gas: 5 per cent. CO_2, 40 per cent. CO, 47 per cent. H_2.

Theoretical data:—

1 vol. gas + 2·5 vols. H_2O.

$a = 0{\cdot}114$, $b = 0{\cdot}714$, $c = 0{\cdot}014$, $d = 0{\cdot}134$.

Temperature.	227°.	327°.	400°.	500°.	600°.
K	0·006	0·03	0·05	0·16	0·32
s	0·1136	0·1129	0·1111	0·1065	0·0997
s/a	0·996	0·990	0·975	0·934	0·875

Experimental data :—

Temperature.	Composition of issuing gas.			y.	y/Y.	Per cent. CO_2.	Per cent. H_2.
	Per cent. CO_2.	Per cent. CO.	Per cent. H_2.			Calculated from y.	
				(*a*) Reduced copper catalyst.			
Composition of gas used :— (i) 150–350° C..... 3·7 per cent. CO_2, 39·6 per cent. CO, 49·0 per cent. H_2. (ii) 400–500° C..... 5·3 per cent. CO_2, 39·0 per cent. CO, 46·7 per cent. H_2.							
150°	3·8	39·2	47·6	0·002	0·005	3·9	49·1
200	4·0	39·4	49·8	0·001	0·002	3·8	49·0
250	9·9	31·2	52·8	0·064	0·162	9·5	52·1
300	14·0	23·7	57·0	0·129	0·326	14·7	54·8
350	17·1	19·9	56·4	0·165	0·416	17·3	56·2
400	15·8	20·3	53·9	0·155	0·398	18·0	54·2
500	18·6	20·3	52·8	0·155	0·398	18·0	54·2
				(*b*) Iron oxide catalyst.			
Composition of gas used :—5·1 per cent. CO_2, 39·9 per cent. CO, 47·3 per cent. H_2.							
200	4·7	39·3	45·0	0·004	0·010	5·5	47·5
250	5·6	36·4	46·7	0·026	0·065	7·5	48·4
300	15·4	23·0	48·3	0·137	0·343	16·0	53·9
350	27·0	7·7	55·4	0·299	0·748	26·9	59·2
400	30·7	5·7	53·1	0·324	0·821	28·3	60·2

The results are given graphically in fig. 2.

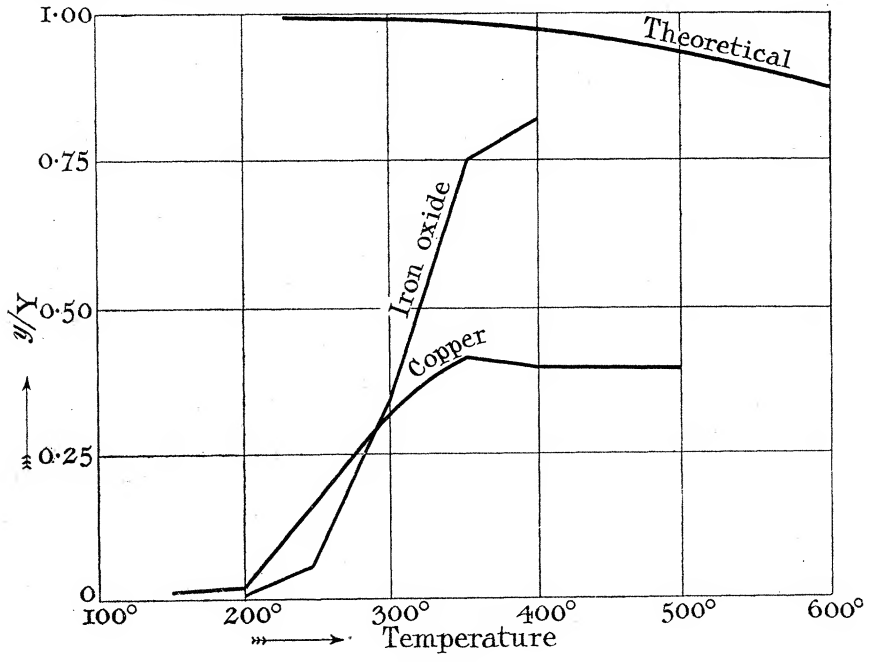

Fig. 2.

Copper is thus much less complete in its action than iron oxide at the higher temperatures; but over the range 200°–300° C. it is definitely more active than iron oxide; copper commences to act at a reasonable rate at about 220° C., whereas iron oxide is barely active at 250° C., is still slow at 300° C. and does not reach full activity until about 400° C.

We have seen that copper decomposes formic acid from 190° C.; on the other hand, the iron oxide process is dependent on the temperature ranges at which oxidation of carbon monoxide by iron oxide and decomposition of steam by iron or ferrous oxide occur at sufficiently rapid rates.

The oxidation of the monoxide by iron oxide proceeds at as low a temperature as 200° C.; but the decomposition of iron by steam is not a rapid action below about 400° C., although this figure refers to massive iron and would no doubt be somewhat lower for the more active iron or ferrous oxide produced by the oxidation of carbon monoxide in presence of steam.

It is evident that the relative activities of (*a*) copper and (*b*) iron oxide to carbon monoxide and steam at the lower ranges of temperature are closely parallel to their respective powers of decomposing (*a*) formic acid and (*b*) steam.

The amount of action effected by the copper catalyst declines somewhat after 350° C., and the maximum change effected appears to be greater the higher the proportion of carbon monoxide in the original gas.

It is not without interest that, although water is not decomposed *per se* by copper, we have observed signs on two occasions that water enters into an active association with this metal, thus :—

(i) The "protective" action of water on aldehyde and the suppression of hydrogenation of aldehyde in presence of water when copper is used as catalyst was explained (this series, Part III) on the hypothesis that water entered into association or was adsorbed preferentially to aldehyde at the copper surface.

(ii) In the present instance, we have a case in which water in association with copper actually takes part in a chemical action.

The following is a summary of the data obtained on passing water-gas (5·1 per cent. CO_2, 39·9 per cent. CO, and 47·3 per cent. H_2) with steam through a tube maintained at 350° C. in presence of ammonia or of lime :—

Experiment.	Alkali present.	Litres of water-gas.		Composition of issuing gas.		
		Passed.	Contraction.	Per cent. CO_2.	Per cent. CO.	Per cent. H_2.
1	Ammonia	50·0	2·15	2·0	37·4	48·5
2	„	50·0	2·85	2·5	37·5	47·3
3	Lime	40·0	2·40	3·1	36·1	50·8

The aqueous condensates from Experiment 2 were made slightly acid with hydrochloric acid and boiled with a solution of mercuric chloride, when 0·0369 gram of mercurous chloride was formed, corresponding to 0·0036 gram of formic acid.

The Theory of the Katharometer.

By H. A. Daynes, M.Sc., University of Birmingham.
(With an Introductory note by G. A. Shakespear.)

(Communicated by Prof. S. W J. Smith, F.R.S. Received January 5, 1920.)

[*Historical Note by G. A. Shakespear, M.A., D.Sc.*—In September, 1915, at the request of a member of the Board of Invention and Research of the Admiralty, I undertook to devise an instrument capable of giving automatic indication of the presence of hydrogen in small quantities (*e.g.*, 1 or 2 per cent.) in air. The well-known surface-action of palladium and platinum wires suggested itself as a phenomenon obviously adapted to the purpose. The wire was used as two arms of a Wheatstone bridge, one of these arms being protected from the gas by a thin glass tube, the other being exposed. When a sufficiently great current of electricity was passed through the bridge, the exposed arm rapidly increased in temperature owing to surface combustion. The temperature, however, was liable to rise dangerously high if the hydrogen were present in suitable quantity, and, as safety from explosion was indispensable, this method was abandoned. The same apparatus was then applied with a much lower current, and with the wires consequently at a much lower temperature, to make use of the increase in thermal conductivity of the gas due to the admixture of hydrogen. This arrangement was found to be unexpectedly sensitive, and the method was adopted for the desired purpose. As the instrument was primarily intended to measure the purity of the air, the name "katharometer" was given to it.

In its final form, the katharometer consisted of two small helices of thin